

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE BEFORE THE
BOARD OF PATENT APPEALS AND INTERFERENCES**

In re Application of: §
Yang et al. §
§ Group Art Unit: 1753
Serial No.: 10/616,044 §
Confirmation No.: 9799 §
§ Examiner: Luan V. Van
Filed: July 8, 2003 §
For: Anolyte for Copper Plating §
§

MAIL STOP: APPEAL BRIEF-PATENTS
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

APPEAL BRIEF

Applicants submit this Appeal Brief to the Board of Patent Appeals and Interferences on appeal from the decision of the Examiner of Group Art Unit 2812 dated December 21, 2005, finally rejecting claims 1-31. The final rejection of claims 1-31 is appealed. This Appeal Brief is believed to be timely since mailed by the due date of May 22, 2006, as set by mailing a Notice of Appeal on March 21, 2006. Authorization to charge the fee of \$500.00 for filing this brief is provided on a separate fee transmittal. Please charge any additional fees that may be required to make this Appeal Brief timely and acceptable to Deposit Account No. 20-0782/007669.P2/KMT.

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Real Party in Interest

The present application has been assigned to Applied Materials, Inc., 3050 Bowers Avenue, Santa Clara, California 95054.

Related Appeals and Interferences

Applicant asserts that no other appeals or interferences are known to the Applicant, the Applicant's legal representative, or assignee which will directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal.

Status of Claims

Claims 1-31 are pending in the application. Claims 1-28 were originally presented in the application. Claims 29-31 were added in Applicants' Response to Office Action dated July 20, 2005. Claims 1-31 stand finally rejected as discussed below. The final rejections of claims 1-31 are appealed. The pending claims are shown in the attached Claims Appendix.

Status of Amendments

All claim amendments have been entered by the Examiner. All claim amendments presented after final rejection have been entered by the Examiner and included in the Claims Appendix.

Summary of Claimed Subject Matter

Claimed embodiments of the invention provide a method for plating copper into features formed on a semiconductor substrate. The method includes positioning the substrate in a plating cell 100, wherein the plating cell 100 includes a catholyte volume containing a catholyte solution, an anolyte volume containing an anolyte solution, an ionic membrane 112 positioned to separate the anolyte volume from the catholyte volume, and an anode 105 positioned in the anolyte volume. The method further includes applying a plating bias between the anode 105 and the substrate, plating copper ions onto the substrate from the catholyte solution, and replenishing the copper ions plated onto the substrate from the catholyte solution with copper ions transported from the anolyte solution via the ionic membrane 112. (See, Abstract, paragraphs 0023-0027, paragraph 0033, and paragraph 0039.)

In the embodiments of independent claim 1, a method is provided for plating metal onto a substrate, the method comprising positioning the substrate in a catholyte solution contained in a catholyte chamber of a plating cell 100, the catholyte solution including an acid source at a concentration of between about 5 g/L and about 15 g/L, a copper source at a concentration of between about 0.8M and about 0.9M, chlorine ions at a concentration of between about 25 ppm and about 75 ppm, and one or more additives (See, paragraphs 0037-0038). The method further includes applying a plating bias between the substrate and an anode 105 positioned in an anolyte chamber of the plating cell 100, the anolyte chamber being separated from the catholyte chamber by an ionic membrane 112 and being supplied with an anolyte solution including a copper source having a concentration of greater than about 51 g/L, wherein the anolyte solution does not contain the one or more additives (See, paragraphs 0034-0035 and paragraphs 0039-0040).

In the embodiments of independent claim 10, a method is provided for plating copper into features formed on a semiconductor substrate, the method comprising positioning the substrate in a plating cell 100, wherein the plating cell 100 includes a catholyte volume containing a catholyte solution, an anolyte volume containing an anolyte solution, wherein the difference between the catholyte solution and the anolyte

solution is that the catholyte solution comprises one or more additives (See, paragraphs 0037-0039), an ionic membrane 112 positioned to separate the anolyte volume from the catholyte volume, and an anode 105 positioned in the anolyte volume (See, Figures 1 and 5, paragraphs 0021-0022, and paragraph 0034). The method further includes applying a plating bias between the anode and the substrate, plating copper ions onto the substrate from the catholyte solution, and replenishing the copper ions plated onto the substrate from the catholyte solution with copper ions transported from the anolyte solution via the ionic membrane 112, wherein the anolyte solution has a copper concentration of greater than about 51 g/L (See, paragraphs 0028, paragraphs 0031-0033, and paragraphs 0039-0040).

In the embodiments of independent claim 19, a method is provided for electrochemically plating copper onto features of a semiconductor substrate, the method comprising positioning the substrate in a plating cell 100 having a catholyte solution volume, an anolyte solution volume, and an ionic membrane 112 separating catholyte solution volume from the anolyte solution volume (See, Figure 1, paragraphs 0023-0024, and paragraphs 0033-0034). The method further includes contacting the substrate with a catholyte solution, applying an electrical bias between the substrate and an anode positioned in the anolyte volume, the electrical bias being sufficient to plate copper ions from the catholyte solution onto the substrate, and replenishing copper ions plated from the catholyte solution via transfer of copper ions from an anolyte solution through the ionic membrane 112 to the catholyte solution (See, paragraphs 0033-0035), the anolyte solution having a pH of between about 2 and about 4.8 and a copper ion concentration of between about 0.1M and about 2M, wherein the difference between the catholyte solution and the anolyte solution is that the catholyte solution comprises one or more additives (See, paragraphs 0039-0040).

In the embodiments of independent claim 25, a method is provided for plating copper onto a substrate, the method comprising positioning the substrate in a catholyte plating solution contained in a catholyte chamber of a plating cell 110, the catholyte plating solution including an acid source at a concentration of between about 5 g/L and about 15 g/L, a copper source at a concentration of between about 0.5M and about

1.0M, chlorine ions at a concentration of between about 25 ppm and about 75 ppm, and one or more additives (See, paragraphs 0037-0038 and paragraphs 0040). The method further includes applying a plating bias between the substrate and an anode 105 positioned in an anolyte chamber of the plating cell 110, the anolyte chamber being separated from the catholyte chamber by an ionic membrane 112 (See, paragraphs 0023-0025), wherein the difference between the catholyte solution and the anolyte solution is that the catholyte solution comprises the one or more additives (See, paragraphs 0034).

In the embodiments of independent claim 29, a method is provided for plating metal onto a substrate, the method comprising positioning the substrate in a catholyte solution contained in a catholyte chamber of a plating cell 110, the catholyte solution comprising a copper source at a concentration of between about 0.8M and about 0.9M and one or more additives (See, paragraphs 0033-0034, and paragraph 0040). The method further includes applying a plating bias between the substrate and an anode 105 positioned in an anolyte chamber of the plating cell 110, the anolyte chamber being separated from the catholyte chamber by an ionic membrane 112 (See, paragraphs 0023-0025) and being supplied with an anolyte solution comprising a copper source at a concentration of greater than about 51 g/L, wherein the ionic membrane 112 is positioned at a vertical position above the anode 105 and in substantially parallel relationship to an upper surface of the anode 105 (See, paragraphs 0028, paragraphs 0031-0033, and paragraphs 0039-0040).

Grounds of Rejection to be Reviewed on Appeal

The Examiner has indicated in the Advisory Action dated March 14, 2006 that Applicant's reply has overcome the 35 U.S.C. §112, first paragraph rejection but not the following rejections as shown in the Final Office Action dated December 21, 2005. The following rejections are appealed.

1. Claims 1-3, 5-10, 13-14, 19-27 and 29 stand rejected under 35 U.S.C. §103(a) as being obvious over *Mayer et al.* (U.S. Patent No. 6,257,920) in view of *Reid et al.* (U.S. Patent Application No. 2001/0015321).
2. Claims 15-16, 28 and 30 stand rejected under 35 U.S.C. §103(a) as being obvious over *Mayer et al.* in view of *Reid et al.*, and further in view of *Woodruff et al.* (U.S. Patent Publication No. 2001/0032788).
3. Claim 4, 11, 12, 17 and 18 stand rejected under 35 U.S.C. §103(a) as being obvious over *Mayer et al.* in view of *Reid et al.*, and further in view of *Dahms et al.* (US Patent No. 6,099,711).
4. Claims 31 stands rejected under 35 U.S.C. §103(a) as being obvious over *Mayer et al.* in view of *Reid et al.*, and further in view of *Sendai et al.* (US Patent Application No. 2003/0057098).

ARGUMENTS

A. Claims 1-3, 5-10, 13-14, 19-27 and 29 are not obvious over *Mayer et al.* in view of *Reid et al.*.

Claims 1-3, 5-10, 13-14, 19-27 and 29 stand rejected under 35 U.S.C. §103(a) as being obvious over *Mayer et al.* in view of *Reid et al.* on grounds that *Mayer et al.* does not teach a copper concentration of between about 0.8 M and about 0.9M in a catholyte and a copper concentration of greater than about 51g/L in an anolyte, but the Examiner states that it would have been obvious where the claimed ranges and the prior art ranges do not overlap but are close enough that one skilled in the art would have expected them to have the same properties. The Examiner also states that *Mayer et al.* discloses a porous membrane 209 and, since the porous membrane of *Mayer et al.* perform the same function as that of the Applicant's membrane, the porous membrane of *Mayer et al.* is an ionic membrane. The Examiner also states that *Mayer et al.* does not explicitly teach the concentration of the chloride ions nor the pH of the anolyte solution, whereas *Reid et al.* teaches a copper source at a concentration of between about 10-60 g/L (or about 0.16-0.94M) and chlorine ions at a concentration of between about 20-200 mg/L (or about 20-2000 ppm), which are within the claimed range. The Examiner asserts that it would have been obvious to one having ordinary skill in the art at the time the invention was made to modify the electroplating method of *Mayer et al.* by the chloride concentration of *Reid et al.*, because such concentration is suitable for electroplating to produce metal films and features. Applicants have respectfully traversed the rejection based on failure of *Mayer et al.* in view of *Reid et al.* to teach or suggest the claimed subject matter.

Mayer et al. discloses an electroplating apparatus including a porous chemical transport barrier 209 between an anode and a cathode to separate an anolyte and a catholyte and prevent mixing thereof. (See, Abstract and Summary.) The porous chemical transport barrier 209 of *Mayer et al.* is not an ionic membrane. The porous chemical transport barrier 209 of *Mayer et al.* limits chemical transport, prevents non-ionic organic species from entering the anolyte, but allows ionic species to pass through. (See, Abstract and column 9, lines 44-52.) Thus, the porous chemical transport

barrier 209 of *Mayer et al.* differentiates ionic species from non-ionic organic species. However, *Mayer et al.* does not teach, show, or suggest any membrane, which differentiates different types of ionic species. An ionic membrane allows only a particular type of ionic species to travel through, while preventing another type of ionic species from traveling or passing through. An ionic membrane may allow positively charged ionic species to pass through, while prevents passage of negatively charged ionic species. Also, an ionic membrane may allow negatively charged ionic species to pass through, while prevents passage of positively charged ionic species. Accordingly, the porous chemical transport barrier 209 of *Mayer et al.* is not an ionic membrane.

In addition, the porous chemical transport barrier 209 of *Mayer et al.* comprises a material including porous glasses, porous ceramics, silica aerogels, organic aerogels, porous polymeric materials, and filter membranes, such as a sintered polyethylene, a sintered polypropylene, a carbon filter layer, or a three-layer membrane including a first layer of porous material sandwiched between two additional layers of porous material. (See, column 4, line 59-67, column 5, lines 1-7.) These materials are not materials for an ionic membrane.

Reid et al. teaches a method of plating copper onto a substrate in a solution without using an ionic membrane. Thus, *Mayer et al.* in view of *Reid et al.*, alone or in combination, does not teach, show, or suggest positioning the substrate in a catholyte solution contained in a catholyte chamber of a plating cell and applying a plating bias between the substrate and an anode positioned in an anolyte chamber of the plating cell, the anolyte chamber being separated from the catholyte chamber by an ionic membrane and being supplied with an anolyte solution, wherein the catholyte solution comprises one or more additives and the difference between the catholyte solution and the anolyte solution is that the catholyte solution comprises the one or more additives, as recited in claims 1, 10, 19, 25, and claims dependent thereon.

Regarding claim 29 and claims dependent thereon, *Mayer et al.* does not teach, show, or suggest any ionic membrane positioned at a vertical position above the anode and in substantially parallel relationship to an upper surface of the anode. *Mayer et al.* in view of *Reid et al.*, alone or in combination, does not teach, show or suggest positioning a substrate in a catholyte solution contained in a catholyte chamber of a

plating cell, the catholyte solution comprising a copper source at a concentration of between about 0.8M and about 0.9M and one or more additives, and applying a plating bias between the substrate and an anode positioned in an anolyte chamber of the plating cell, the anolyte chamber being separated from the catholyte chamber by an ionic membrane and being supplied with an anolyte solution comprising a copper source at a concentration of greater than about 51 g/L, wherein the ionic membrane is positioned at a vertical position above the anode and in substantially parallel relationship to an upper surface of the anode, as recited in claim 25 and claims dependent thereon. Accordingly, withdrawal of the rejection and allowance of claims 1, 10, 19, 25 and 29, and claims dependent thereon are respectfully requested.

B. Claims 15-16, 28 and 30 are not obvious over *Mayer et al.* in view of *Reid et al.*, and further in view of *Woodruff et al.*.

Claims 15-16, 28 and 30 stand rejected under 35 U.S.C. §103(a) as being obvious over *Mayer et al.* in view of *Reid et al.*, and further in view of *Woodruff et al.* on grounds that *Mayer et al.* does not teach an electroplating method, wherein an ionic membrane comprises a fluorized polymer matrix or a polydivinilbenzol matrix, whereas *Woodruff et al.* teaches a NAFION perfluorinated membrane, and it would have been obvious to modify the electroplating method of *Mayer et al.* in view of *Reid et al.* by using the membrane of *Woodruff et al.*, because the perfluorinated membrane would reduce the consumption of additives. Applicants have respectfully traversed the rejections based on the failure of *Mayer et al.* in view of *Reid et al.*, and further in view of *Woodruff et al.* to teach or suggest the claimed subject matter.

Mayer et al. and *Reid et al.* have been discussed above.

Woodruff et al. discloses an electrochemical processing chamber 200 and an interface member 700, which is a filter or ion-membrane designed to be positioned vertically in order to allow a secondary fluid flow F₂ to pass and join a primary fluid flow F_p, and prevent bubbles from the secondary fluid flow F₂ to pass, forcing bubbles in the secondary fluid flow F₂ to rise. (See, paragraphs 81, 83, 86-89.) When the interface member 700 is an ion-membrane, it prevents particles, organic additives, and bubbles

in the secondary fluid flow F_2 to pass through into the primary fluid flow F_p and eliminates the consumption of the additives at the anode and the need to replenish the additives at the anode because the additives supplied to the secondary fluid flow F_2 , which can be an anolyte, do not affect the primary fluid flow F_p . (See, paragraphs 88-89.) Thus, the anolyte of *Woodruff et al.* in the secondary fluid flow F_2 includes additives and can not be passed through into the primary fluid flow F_p . *Woodruff et al.* does not describe the difference between a catholyte solution and an anolyte solution is that the catholyte solution comprises one or more additives.

Neither *Mayer et al.*, *Reid et al.*, nor *Woodruff et al.* discloses an ionic membrane, a catholyte solution comprising additives, and an anolyte solution comprising no additives. There is no motivation to include an ionic membrane which separates an anolyte volume containing an anolyte solution without additives from a catholyte volume containing a catholyte solution with additives, from the combination of *Mayer et al.*, *Reid et al.*, and *Woodruff et al.* Accordingly, *Mayer et al.* in view of *Reid et al.*, and further in view of *Woodruff et al.*, alone or in combination, does not disclose or suggest a plating cell including an ionic membrane positioned to separate an anolyte volume from a catholyte volume and a difference between a catholyte solution and an anolyte solution is that the catholyte solution comprises one or more additives.

Applicant asserts that the Examiner has not supplied the requisite motivation from the combination of references to combine the teachings of *Mayer et al.*, which discloses a catholyte solution comprises organic additives and an anolyte solution comprises no organic additives, with the teachings of *Woodruff et al.*, which discloses an ionic membrane to separate two fluid flows that both contain additives. Applicant submits that “[t]he showing of a motivation to combine must be clear and particular, and it must be supported by actual evidence. *In re Dembiczak*, 50 U.S.P.Q. 2d 1614, 1617 (Fed. Cir. 1999).

The Examiner has failed to show a clear and particular motivation by the skilled artisan to select from the combined disclosures of *Mayer et al.* with *Reid et al.* and *Woodruff et al.* On this point, the Federal Circuit has ruled that “[o]ne cannot use hindsight reconstruction to pick and choose among isolated disclosures in the prior art to deprecate the claimed invention.” (*In re Fritch* at 1784). In order to avoid using the

Applicant's disclosure as a blueprint to pick and choose certain elements, while ignoring others, the Examiner must supply a clear and particular motivation or suggestion to do so. In the present case, the only suggestion is provided in the Applicant's disclosure and thus hindsight.

Furthermore, the compositions, methods or steps of *Mayer et al.*, *Reid et al.* and *Woodruff et al.* are each distinctly described and, in combination, provide no suggestion, motivation, or expectation of success for the claimed subject matter. Therefore, *Mayer et al.* in view of *Reid et al.*, and further in view of *Woodruff et al.*, alone or in combination, do not teach, show, or suggest positioning the substrate in a plating cell, wherein the plating cell includes a catholyte volume containing a catholyte solution, an anolyte volume containing an anolyte solution, an ionic membrane positioned to separate the anolyte volume from the catholyte volume, and an anode positioned in the anolyte volume, applying a plating bias between the anode and the substrate, plating copper ions onto the substrate from the catholyte solution, and replenishing the copper ions plated onto the substrate from the catholyte solution with copper ions transported from the anolyte solution via the ionic membrane, wherein the anolyte solution has a copper concentration of greater than about 51 g/L and the difference between the catholyte solution and the anolyte solution is that the catholyte solution comprises one or more additives, as recited in claims 10, 25, which claims 15-16, 28 and 30 are dependent thereon. Withdrawal of the rejection is respectfully requested.

C. Claims 4, 11, 12, 17 and 18 are not obvious over *Mayer et al.* in view of *Reid et al.*, and further in view of *Dahms et al.*.

Claims 4, 11, 12, 17 and 18 stand rejected under 35 U.S.C. §103(a) as being obvious over *Mayer et al.* in view of *Reid et al.*, and in further view of *Dahms et al.* on grounds that *Mayer et al.* do not teach an electroplating method wherein the accelerator comprises sulfo propyldisulfide and *Dahms et al.* teaches an electroplating method for copper having an accelerator comprising of bis-(w-sulfopropyl)-disulfide, disodium salt (Table 2). Applicants have respectfully traversed the rejection based on the failure of

Mayer et al. in view of *Reid et al.*, and in further view of *Dahms et al.* to teach or suggest the claimed subject matter.

Mayer et al. and *Reid et al.* have been discussed above.

Dahms et al. teaches an electrolytic method for plating copper on printed circuit boards by applying current pulse or voltage pulse and adding additives such as oxygen-containing, high molecular weight compounds and sulfur compounds with appropriate functional groups, such as bis-(w-sulfopropyl)-disulfide, disodium salt. *Dahms et al.* does not teach, show or suggest an ionic membrane. *Mayer et al.* in view of *Reid et al.*, and in further view of *Dahms et al.*, alone or in combination, does not teach, show or suggest an anolyte chamber being separated from a catholyte chamber by an ionic membrane, as recited in claims 1, 10, which claims 4, 11, 12, 17 and 18 are dependent thereon.

Accordingly, *Mayer et al.* in view of *Reid et al.*, and further in view of *Dahms et al.*, alone or in combination, does not teach, show, or suggest positioning the substrate in a catholyte solution contained in a catholyte chamber of a plating cell and applying a plating bias between the substrate and an anode positioned in an anolyte chamber of the plating cell, the anolyte chamber being separated from the catholyte chamber by an ionic membrane and being supplied with an anolyte solution, wherein the catholyte solution comprises one or more additives and the difference between the catholyte solution and the anolyte solution is that the catholyte solution comprises the one or more additives, as recited in claims 1, 10, and claims dependent thereon. Withdrawal of the rejection is respectfully requested.

D. Claim 31 is not obvious over *Mayer et al.* in view of *Reid et al.*, and further in view of *Sendai et al.*.

Claim 31 stands rejected under 35 U.S.C. §103(a) as being obvious over *Mayer et al.* in view of *Reid et al.*, and further in view of *Sendai et al.* on grounds that *Mayer et al.* does not teach tilting the anode and *Sendai et al.* teaches a method and apparatus for tilting the anode at an angle from 1-10° with respect to a horizontal plane and it would have been obvious to one having ordinary skill in the art at the time the invention was made to modify the electroplating method of *Mayer et al.* by tilting the anode as

taught by *Sendai et al.* Applicants have respectfully traversed the rejection based on the failure of *Mayer et al.* in view of *Reid et al.*, and further in view of *Sendai et al.* to teach or suggest the claimed subject matter.

Mayer et al. and *Reid et al.* have been discussed above.

Sendai et al. discloses an electro-chemical plating system having a tilt mechanism and a head portion for holding a substrate, and a method of immersing the wafer by tilting the substrate in an inclined angle of α which is 1° to 10° . (See, Figures 1-9 and paragraphs 0022-0025.) *Sendai et al.* also discloses that, after the surface of the substrate is immersed into a plating solution of a plating cell, the substrate is brought back to a horizontal position for processing the substrate, when the plating cell is stationed horizontally. (See, Figures 3-4 paragraphs 0022-0025 and 0080-0087.) Alternatively, when the plating cell and the anode therein is stationed at an inclined angle of β , *Sendai et al.* discloses tilting the substrate in an inclined angle of β before and after the surface of the substrate is immersed into a plating solution of a plating cell without having to bring the substrate back to horizontal such that the substrate and the plating cell are tilted at the same inclined angle of β during both immersion and plating processes. (See, Figures 11-12 and paragraphs 0091-0096.) *Sendai et al.* does not teach, show, or suggest an ionic membrane, as lacking in *Mayer et al.* in view of *Reid et al.* In addition, *Sendai et al.* does not teach, show, or suggest separating an anolyte chamber from a catholyte chamber by the ionic membrane, wherein the ionic membrane is positioned at a vertical position above the anode and in substantially parallel relationship to an upper surface of the anode, which is also lacking in *Mayer et al.* in view of *Reid et al.* In addition, there is no suggestion or motivation in the combination of the references to combine the references.

Accordingly, *Mayer et al.* in view of *Reid et al.*, and further in view of *Sendai et al.*, alone or in combination, do not teach, show, or suggest positioning a substrate in a catholyte solution contained in a catholyte chamber of a plating cell, the catholyte solution comprising a copper source at a concentration of between about 0.8M and about 0.9M and one or more additives, and applying a plating bias between the substrate and an anode positioned in an anolyte chamber of the plating cell, the anolyte chamber being separated from the catholyte chamber by an ionic membrane and being

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supplied with an anolyte solution comprising a copper source at a concentration of greater than about 51 g/L, wherein the ionic membrane is positioned at a vertical position above the anode and in substantially parallel relationship to an upper surface of the anode, as recited in claim 29, which claim 31 is dependent thereon. Withdrawal of the rejection is respectfully requested.

CONCLUSION

The Examiner errs in finding that it would have been obvious to use a porous membrane and a plating method as taught by *Mayer et al.* in a plating process as disclosed by *Reid et al.* to reject claims 1-3, 5-10, 13-14, 19-27 and 29, because *Mayer et al.* in view of *Reid et al.*, alone or in combination, does not teach, show, or suggest an ionic membrane.

The Examiner also errs in finding that it would have been obvious to modify a plating method as taught by *Mayer et al.* in view of *Reid et al.* by using the membrane of *Woodruff et al.* to reject claims 15-16, 28, and 30, because *Mayer et al.* in view of *Reid et al.*, and in further view of *Woodruff et al.*, alone or in combination, does not teach, show, or suggest a plating cell including an ionic membrane positioned to separate an anolyte volume from a catholyte volume, wherein a difference between a catholyte solution and an anolyte solution is that the catholyte solution comprises one or more additives.

The Examiner also errs in finding that it would have been obvious to modify the combined method of *Mayer et al.* and *Reid et al.* by using the accelerator of *Dahms et al.* to reject claims 4, 1-12, and 17-18, because *Mayer et al.* in view of *Reid et al.*, and in further view of *Dahms et al.*, alone or in combination, does not teach, show, or suggest an anolyte chamber being separated from a catholyte chamber by an ionic membrane.

The Examiner further errs in finding that it would have been obvious to modify the electroplating method of *Mayer et al.* and *Reid et al.* by tilting the anode as taught by *Sendai et al.*, to reject claims 31, because *Mayer et al.* in view of *Reid et al.*, and in further view of *Sendai et al.*, alone or in combination, does not teach, show, or suggest an ionic membrane, nor separating an anolyte chamber from a catholyte chamber by the ionic membrane, wherein the ionic membrane is positioned at a vertical position above the anode and in substantially parallel relationship to an upper surface of the anode.

Respectfully submitted,



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CLAIMS APPENDIX

1. (Previously Presented) A method for plating metal onto a substrate, comprising:

positioning the substrate in a catholyte solution contained in a catholyte chamber of a plating cell, the catholyte solution comprising:

an acid source at a concentration of between about 5 g/L and about 15 g/L;

a copper source at a concentration of between about 0.8M and about 0.9M;

chlorine ions at a concentration of between about 25 ppm and about 75 ppm; and

one or more additives; and

applying a plating bias between the substrate and an anode positioned in an anolyte chamber of the plating cell, the anolyte chamber being separated from the catholyte chamber by an ionic membrane and being supplied with an anolyte solution comprising a copper source having a concentration of greater than about 51 g/L, wherein the anolyte solution does not contain the one or more additives.

2. (Previously Presented) The method of claim 1, wherein the one or more additives in the catholyte solution comprises:

a leveler at a concentration of between about 2 mL/L and about 3 mL/L;

a suppressor at a concentration of between about 2 mL/L and about 3 mL/L; and

an accelerator at a concentration of between about 5.5 mL/L and about 8 mL/L.

3. (Previously Presented) The method of claim 2, wherein the suppressor comprises a compound selected from the group consisting of ethylene oxide, propylene oxide, and combinations thereof.

4. (Original) The method of claim 2, wherein the accelerator comprises sulfo propyldisulfide.
5. (Original) The method of claim 1, wherein the anolyte has a pH of between about 2 and about 4.8.
6. (Original) The method of claim 5, wherein the anolyte comprises a copper II salt having a concentration of copper ions of between about 0.1M and about 2M.
7. (Previously Presented) The method of claim 6, wherein the copper II salt comprises a compound selected from the group consisting of copper sulfate, copper sulfonate, copper chloride, copper nitrate, and blends thereof.
8. (Original) The method of claim 5, wherein the anolyte provides a copper transport of copper ions through the ionic membrane of between about 90% and about 100%.
9. (Previously Presented) The method of claim 1, wherein the anode is selected from the group consisting of a copper anode, a platinum anode, and combinations thereof.
10. (Previously Presented) A method for plating copper into features formed on a semiconductor substrate, comprising:
 - positioning the substrate in a plating cell, wherein the plating cell comprises:
 - a catholyte volume containing a catholyte solution;
 - an anolyte volume containing an anolyte solution, wherein the difference between the catholyte solution and the anolyte solution is that the catholyte solution comprises one or more additives;

an ionic membrane positioned to separate the anolyte volume from the catholyte volume; and

an anode positioned in the anolyte volume;

applying a plating bias between the anode and the substrate;

plating copper ions onto the substrate from the catholyte solution; and

replenishing the copper ions plated onto the substrate from the catholyte solution with copper ions transported from the anolyte solution via the ionic membrane, wherein the anolyte solution has a copper concentration of greater than about 51 g/L.

11. (Original) The method of claim 10, wherein the copper concentration is supplied by copper sulfate pentahydrate having a molarity of between about 0.8M and about 0.9M.

12. (Previously Presented) The method of claim 11, wherein the anolyte solution has a pH of between about 2 and 4.8.

13. (Original) The method of claim 10, wherein the plating cell further comprises a diffusion member positioned between an upper surface of the ionic membrane and the substrate.

14. (Original) The method of claim 13, wherein the diffusion member comprises a porous ceramic disk.

15. (Original) The method of claim 10, wherein the ionic membrane comprises a membrane having a fluorized polymer matrix.

16. (Original) The method of claim 10, wherein the ionic membrane comprises a membrane having a polydivinilbenzol matrix.

17. (Previously Presented) The method of claim 12, wherein the catholyte solution comprises:

acid at a concentration of between about 5 g/L and about 15 g/L;
copper at a concentration of between about 0.8M and about 0.9M; and
chlorine ions at a concentration of between about 25 ppm and about 75 ppm.

18. (Previously Presented) The method of claim 17, wherein the one or more additives in the catholyte solution further comprises:

a leveler at a concentration of between about 2 mL/L and about 3 mL/L;
a suppressor at a concentration of between about 2 mL/L and about 3 mL/L; and
an accelerator at a concentration of between about 5 mL/L and about 8 mL/L.

19. (Previously Presented) A method for electrochemically plating copper onto features of a semiconductor substrate, comprising:

positioning the substrate in a plating cell having a catholyte solution volume, an anolyte solution volume, and an ionic membrane separating catholyte solution volume from the anolyte solution volume;

contacting the substrate with a catholyte solution;

applying an electrical bias between the substrate and an anode positioned in the anolyte volume, the electrical bias being sufficient to plate copper ions from the catholyte solution onto the substrate; and

replenishing copper ions plated from the catholyte solution via transfer of copper ions from an anolyte solution through the ionic membrane to the catholyte solution, the anolyte solution having a pH of between about 2 and about 4.8 and a copper ion concentration of between about 0.1M and about 2M, wherein the difference between the catholyte solution and the anolyte solution is that the catholyte solution comprises one or more additives.

20. (Original) The method of claim 19, wherein the copper ion concentration in

the anolyte comprises between about 51 g/L and about 60 g/L of copper metal to the anolyte.

21. (Original) The method of claim 19, wherein the anolyte provides a copper transport of copper ions through the ionic membrane of between about 90% and about 100%.

22. (Previously Presented) The method of claim 19, wherein the catholyte solution volume comprises:

an acid source at a concentration of between about 5 g/L and about 15 g/L;
a copper source at a concentration of between about 0.8M and about 0.9M; and
chlorine ions at a concentration of between about 25 ppm and about 75 ppm.

23. (Previously Presented) The method of claim 22, wherein the one or more additives in the catholyte further comprises:

a leveler at a concentration of between about 2 mL/L and about 4 mL/L;
a suppressor at a concentration of between about 1.5 mL/L and about 3 mL/L;
and
an accelerator at a concentration of between about 5.5 mL/L and about 8 mL/L.

24. (Previously Presented) The method of claim 23, wherein the anode is selected from the group consisting of a copper anode, a platinum anode, and combinations thereof.

25. (Previously Presented) A method for plating copper onto a substrate, comprising:

positioning the substrate in a catholyte plating solution contained in a catholyte chamber of a plating cell, the catholyte plating solution comprising:

an acid source at a concentration of between about 5 g/L and about 15 g/L;

a copper source at a concentration of between about 0.5M and about 1.0M;

chlorine ions at a concentration of between about 25 ppm and about 75 ppm; and

one or more additives; and

applying a plating bias between the substrate and an anode positioned in an anolyte chamber of the plating cell, the anolyte chamber being separated from the catholyte chamber by an ionic membrane, wherein the difference between the catholyte solution and the anolyte solution is that the catholyte solution comprises the one or more additives.

26. (Original) The method of claim 25, wherein the anolyte comprises a copper source having a concentration of greater than about 51 g/L.

27. (Original) The method of claim 26, wherein the anolyte has a pH of between about 2 and about 4.8.

28. (Original) The method of claim 26, wherein the ionic membrane comprises a membrane having a polydivinilbenzol matrix.

29. (Previously Presented) A method for plating metal onto a substrate, comprising:

positioning the substrate in a catholyte solution contained in a catholyte chamber of a plating cell, the catholyte solution comprising a copper source at a concentration of between about 0.8M and about 0.9M and one or more additives; and

applying a plating bias between the substrate and an anode positioned in an anolyte chamber of the plating cell, the anolyte chamber being separated from the catholyte chamber by an ionic membrane and being supplied with an anolyte solution comprising a copper source at a concentration of greater than about 51 g/L, wherein the

ionic membrane is positioned at a vertical position above the anode and in substantially parallel relationship to an upper surface of the anode.

30. (Previously Presented) The method of claim 29, wherein the ionic membrane comprises a membrane having a polydivinilbenzol matrix.

31. (Previously Presented) The method of claim 29, wherein the upper surface of the anode is tilted between about 3° and about 30° from horizontal.